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Recycle of Valuable Metals in Converter Steel Slag for Preparing Multidoped $M_xMg_{1-x}Fe_2O_4$ (M = Mn, Ca) Spinel

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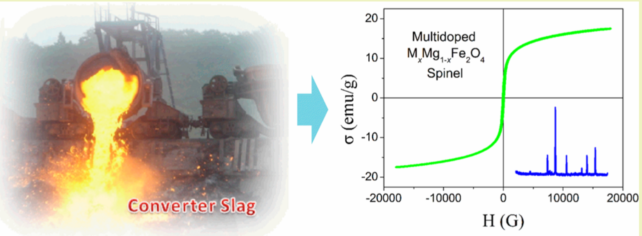
ABSTRACT: A new route for preparing multidoped spinels $M_xMg_{1-x}Fe_2O_4$ (M = Mn, Ca) by using converter steel slag as raw materials is proposed in this study. All of Mg, Fe, M, and dopants used to prepare $M_xMg_{1-x}Fe_2O_4$ were simultaneously recovered from the slag. The results indicate that the slag-derived $M_xMg_{1-x}Fe_2O_4$ exhibited a single-phase spinel and when calcined at 1000 °C gave a saturation magnetization of 17.48 emu/g.



KEYWORDS: *Converter steel slag, Recycling, Precipitation, Multidoping, Magnetic materials*

■ INTRODUCTION

Converter steel slag, a large-scale byproduct generated in the steelmaking process, contains a large amount of Fe, various valuable elements such as Mg, Mn, Cr, Al, and other heavy metals, being actually a potential secondary resource. However, the effective utilization rate of this slag is only about 20% due to the complexity of its composition. Increasing slag heaps resulted in not only environmental pollution but also waste of the resource.[1,2] Previous studies on effective utilization of converter steel slag usually were focused on its recycling in steelmaking, Portland cement production, and road construction.[3,4] However, these strategies have been hindered by some functional, economical, and ecological problems due to neglect of multiple metals recovery. Apparently, recovery of these valuable metals and conversion of them into some high-added-value materials is a key to advance the effective utilization of converter slag. Fortunately, such a topic has been attracting more and more attention in recent years.[5−8] Containing a large amount of Fe, Mg, and many valuable metals (Mn, Cr, Ti, V, etc.), converter steel slag is actually a potential source of Fe, Mg, and multiple dopants for preparing multidoped $M_xMg_{1-x}Fe_2O_4$, but such a strategy is seldom reported.

Spinel of the type $M^{2+}M^{3+}{}_2O_4$ has attracted growing interest worldwide because of its extensive applications,[9,10] such as $MgFe_2O_4$. In the case of $M^{3+} = Fe^{3+}$, the spinel ferrites with a general chemical formula of MFe_2O_4 (M = Mn, Mg, Zn, Ni, Ca, etc.) are most widely used among magnetic materials.[11] Traditionally, almost all spinel ferrites were synthesized using chemical reagents as raw materials,[12] but more sustainable routes are now being used, like conversion of waste into ferrites.[13,14] In the present work, we conduct a new method for conversion of converter steel slag into multidoped $M_xMg_{1-x}Fe_2O_4$ spinel, with the intent to discover a sustainable route for effective utilization of converter steel slag.

■ EXPERIMENTAL SECTION

The as-received converter steel slag (from Maanshan Iron & Steel Company Limited of China, shown in Table 1) was dried at 110 °C for 12 h and ground to 2 mm. Twenty grams of treated slag powder was added into 400 mL of sulfuric acid solution (1.5 M) in a beaker placed in an 85 °C water bath, with stirring for 2 h. After completion of the reaction and filtration, the target elements (Fe, Mg, Mn, Cr, etc.) were transferred from the slag into the filtrate in the form of sulfates. Most of Ca in the slag was changed into filter residue as a calcium sulfate precipitates, and only a some of the Ca were transferred into the filtrate. Heating the filtrate to 85 °C and holding for 4 h, silica gel formed and was filtrated out, and the target filtrate containing all the desirable elements was obtained. Subsequently, H_2O_2 (30%) and NaOH (2.5 M) were successively dripped into the filtrate under stirring, and a red-brown precipitate was formed. Then, the precipitate was rinsed several times with deionized water and dried in an oven at 100 °C for 12 h to form precursors. The precursors were calcined in air atmosphere at 500, 600, 700, 800, 900, 1000, and 1100 °C for 2 h, and multidoped $M_xMg_{1-x}Fe_2O_4$ spinel samples were finally obtained. Generally, 8.2 g of the $M_xMg_{1-x}Fe_2O_4$ sample can be obtained from 20 g of slag, and the conversion ratio of material slag to the final product is about 41%.

X-ray fluorescence (XRF, ARL-9800, Switzerland) was used for the determination of the element content in the slag and precursors. Thermo-gravimetric and differential thermal analysis were carreid out on a thermal analyzer (TG-DTA, DTG-60H, Japan). X-ray diffraction (XRD, D8 Advance, Bruker AXS) using Cu Kα radiation was employed to identify the crystalline phase of the calcined samples. The conventional vibrating sample magnetometer (Lakeshore 7300) was used to measure the magnetic properties of materials at room temperature with the applied field from −20000 to 20000 G. The particle sizes of samples were analyzed by laser particle size analyzer (Malvern Zeta-sizer Ver. 6.01, Britain).

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Table 1. Chemical Composition of the Converter Steel Slag (wt %)

compounds	Fe_2O_3	CaO	MgO	SiO_2	MnO	TiO_2	Al_2O_3	P_2O_5	Cr_2O_3	others
content	30.27	47.05	4.77	9.77	2.99	0.571	1.96	1.46	0.150	1.009

Table 2. Chemical Composition of the Precursors Obtained from Co-Precipitation at Different pH

element	pH	Fe	Mg	Mn	Cr	Al	Si	P	Ca	O
weight %	9	47.84	6.21	4.05	0.24	0.82	0.43	0.51	2.01	37.89
	10	48.64	6.92	4.14	0.25	0.85	0.47	0.54	3.30	34.89
atom %	9	22.76	6.93	1.90	0.11	0.81	0.41	0.28	1.34	64.56
	10	24.47	8.12	2.12	0.13	0.88	0.47	0.31	2.04	61.46

RESULTS AND DISCUSSION

As shown in Table 1, the main components Ca (CaO), Fe (Fe_2O_3), Mg (MgO), Mn (MnO) in the slag accounted for 47.05, 30.27, 4.77, and 2.99 wt %, respectively. Al, Cr, Ti, and other useful metal elements are rare or microcomponents. Fe, Mg, Mn, and some Ca are essential elements for preparing multidoped $M_xMg_{1-x}Fe_2O_4$, and Al, Cr, Ti, etc. can be served as doping elements to improve the magnetic properties and catalytic performance.[15−18] Therefore, Fe, Mg, Mn, Al, Cr, and Ca in the converter steel slag were identified as target elements for preparing multidoped $M_xMg_{1-x}Fe_2O_4$ in this work. Actually, most of the Ca could be removed by sulfolysis of converter slag and filtration, and only some Ca transferred into the filtrate along with other target elements, which could meet the dosage of Ca for substituting for partial Mg in the synthesis of multidoped $M_xMg_{1-x}Fe_2O_4$.[19]

The composition of the slag-derived $M_xMg_{1-x}Fe_2O_4$ precursors is given in Table 2. When pH value increased from 9 to 10, the contents of Fe^{3+}, Mn^{2+}, Al^{3+}, and Cr^{3+} in the precursors were nearly constant, but those of Fe^{3+}, Mg^{2+}, and Ca^{2+} were evidently increased, indicating that a higher pH value than 9 is needed for complete precipitation of Mg^{2+} and Ca^{2+}. At pH 10, the molar ratio of Fe to Mg + Mn + Ca in the precursor is very close to 2, which meets the requirement of the chemical formula $M_xMg_{1-x}Fe_2O_4$.

The TG-DTA curve (Figure 1) indicates that three main weight losses occurred on the TG curve from room temperature to 490 °C, which correspond to three endothermic peaks on the DTA profile, revealing the escape of freedom water, constitutional water, and decomposition of some hydroxyl-bearing intermediates.[20] Continuing to increase the temperature to 1100 °C, a broad exothermic phenomenon presents on the DTA curve from 490 to 1080 °C with only a little weight loss on the TG curve, which may be ascribed to a further decomposition of some intermediates. These phenomena may imply that a crystallization of the precursor from an amorphous mixture to crystalline spinel $M_xMg_{1-x}Fe_2O_4$ should take place above 490 °C, and this deduction is supported by the succedent XRD analyses.

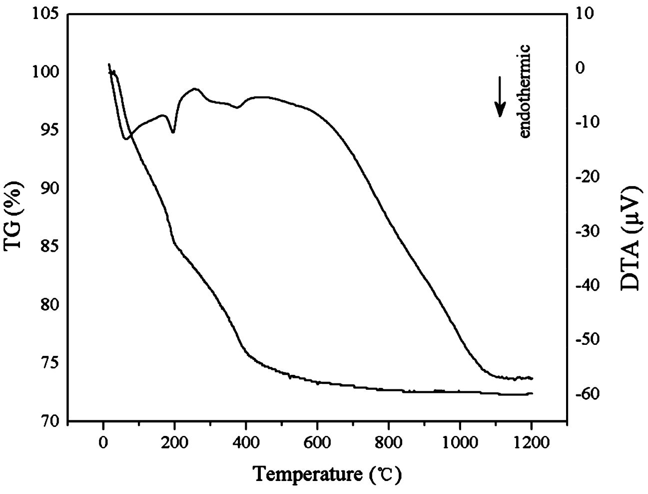

Figure 1. TG-DTA curve of the slag-derived precursor precipitated at pH 10.

Figure 2 shows the X-ray diffraction patterns of the samples calcined at different temperatures. No observable characteristic peaks appear on the XRD patterns of 500 °C sample, indicating that the precursor is still amorphous when heating to 500 °C. Heating to 600 °C, a weak crystallization takes place, and the crystallization gradually strengthens with increasing calcining temperature to 800 °C. The obvious characteristic peaks, which can be indexed as the cubic spinel type $MgFe_2O_4$ (JCPDS 36-0398), can be observed from the XRD patterns of the 900 °C sample, and those gradually strengthen from 900 to 1000 and 1100 °C. The results indicate that a single-phase spinel was successfully synthesized by calcining the slag-derived precursor above 900 °C.

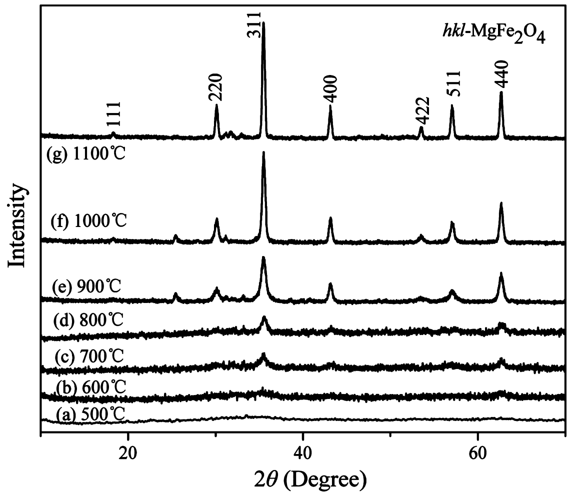

Figure 2. XRD patterns of the samples produced by calcining the slag-derived precursor at different temperature.

The hysteresis loops of samples calcined at different temperatures for 2 h are shown in Figure 3(a). All three samples show an obvious ferromagnetic behavior. The saturation magnetization of spinel $M_xMg_{1-x}Fe_2O_4$ samples calcined at 900, 1000, and 1100 °C are 10.62, 17.48, and 8.05 emu/g, respectively. The calcining temperatures have a very

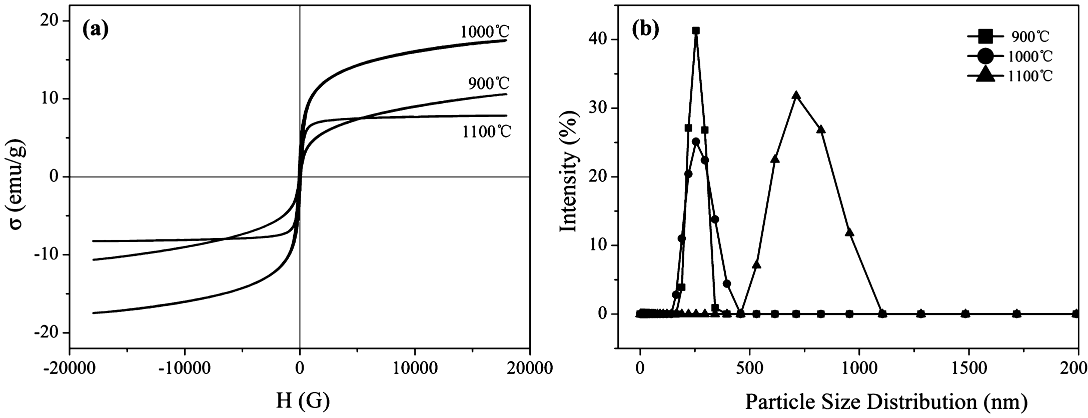

Figure 3. (a) Hysteresis loops for materials produced by calcinations. (b) Particle size distributions of samples calcined at different temperatures.

large effect on the saturation magnetization of the samples due to their influence on the crystal's formation, grain sizes, and specific surface of the material.[21] The particle size distributions of the tested samples are given in Figure 3(b). The difference of particle sizes between the 900 and 1000 °C samples is unconspicuous, so their magnetic performances should be mainly related to the cubic spinel type transformation (Figure 2). The particle size of 1100 °C samples is much larger than that of the 1000 °C sample, resulting in a sharp decrease in the saturation magnetization of the 1100 °C samples. In addition, saturation magnetization of the slag-derived $M_xMg_{1-x}Fe_2O_4$ spinels are lower than those of pure $MgFe_2O_4$ produced by conventional ceramic (26.40 emu/g) and wet chemical (26.60 emu/g) methods at 1100 °C for 10 h.[22] The detailed reasons and further improvements of the product's magnetic performance will be studied in our future work.

In conclusion, we report herein, for the first time, on a feasible route for recovery of multiple elements existing in converter steel slag to synthesize multidoped $M_xMg_{1-x}Fe_2O_4$ spinel. All elements used for preparing $M_xMg_{1-x}Fe_2O_4$ are recovered from the slag, without addition of any chemicals as raw materials. The results suggest that converter steel slag could be used as a more economical and ecological substitute for chemicals to produce magnetic spinel materials. Furthermore, the residues after acidolysis of metals from the slag, for example, calcium sulfate, are appropriate for application in cement production and other civil construction.

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Notes

The authors declare no competing financial interest.

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